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Redox-isomerism in main group chemistry: tin complex with *o*-iminoquinone ligands

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Abstract: Bis-chelate tin complex **1** on the basis of 4,6-di-*tert*-butyl-*N*-(*tert*-butyl)-*ortho*-aminophenol ligand representing the first example of redox-isomeric compound in main group chemistry was synthesized and characterized by X-ray analysis. It was found that **1** exists in two electromeric forms in non-polar solvents: diamagnetic pseudotetrahedral $(AP)_2Sn^{IV}$ (**1a**) and paramagnetic tetragonal-pyramidal structure of low-valence tin $(imSQ)_2Sn^{II}$ (**1b**) (where AP and imSQ – dianion and radical-anion forms of the ligand, respectively). The reversible redox-isomeric rearrangement between **1a** and **1b** was investigated in solution by means of magnetochemistry, EPR, UV-Vis and ^{119}Sn Mössbauer spectroscopy. This interconversion can be quenched by an addition of strong donor ligand such as pyridine (Py), resulting in an octahedral complex $(AP)_2Sn^{IV}(Py)_2$ (**2**) which does not undergo redox-isomerism.

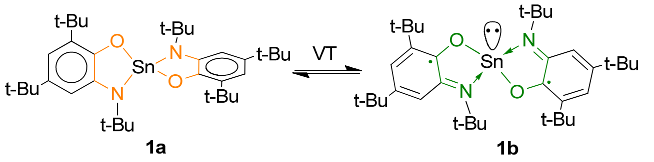
Introduction

Transition metal complexes may exhibit thermally or light-induced reversible intramolecular electron transfer between a metal centre and a redox-active ligand (or ligands) giving rise to two isomers. This effect is called redox-isomerism (or valence tautomerism) and was firstly reported by Pierpont and Buchanan in 1980 for substituted *o*-benzoquinone complex of cobalt.[1] Since rearrangements of this type are usually accompanied by a change in the systems spin state, complexes capable of valence tautomerism (VT) represent promising candidates for the design of molecular switches with magnetic responses.[2] To date, the synthesis and VT behaviour of transition metal (V, Mn, Fe, Co, Ni, Cu and Ru) coordination compounds with a variety of redox-active ligand types including *o*-quinones, *o*-iminoquinones and α-diimines have been extensively studied and amply reviewed.[3] Rare examples of redox-isomerism in lanthanide (Yb) complexes of diiminoacenaphthene ligand were reported recently.[4]

The search for a unique phenomenon of redox-isomerism in non-transition metal complexes represents a challenge. To the best of our knowledge, reversible valence-tautomeric rearrangement, involving a main group metal centre and redox-active ligands, was not observed. An example of the solvent-induced metal–metal bond dissociation supported by electron transfer to the organic ligands was found in gallium complex bearing diiminoacenaphthene.[5] It should be noted that this process is irreversible and accompanied with chemical transformation.

Ligand-based redox-isomerism in zinc compound $Zn(L)_2$ bearing tridentate *o*-iminoquinone ligands has been reported by Wieghardt et al.[6] However further theoretical investigations have shown that it is neither metal-to-ligand nor ligand-to-ligand electron transfer and most likely this transformation is caused by singlet-triplet transition of one of the redox-active ligands.[7]

Recently, we reported a quantum chemical investigation of the possibility of the occurrence of VT in group 14 (E = Si, Ge, Sn, Pb) element derivatives with redox-active *o*-indophenols and *o*-aminophenols.[8] It was shown that bis-chelate tin complex **1** on the basis of 4,6-di-*tert*-butyl-N-(*tert*-butyl)-*o*-aminophenol is characterized by a narrow energy gap (7.0 kcal·mol^{-1}) between the pseudotetrahedral **1a** and tetragonal-pyramidal **1b** electromeric[9] forms and a low energy barrier for their interconversion (11.7 kcal·mol^{-1}). Noteworthy that according to the calculations diradical tin(II) structure **1b** is a ground state with respect to the pseudotetrahedral diamagnetic **1b**. Thus, data obtained allow us to consider compound **1** as a promising candidate for the observation of thermally driven redox-isomeric rearrangement (Scheme 1).



Scheme 1. Reversible redox-isomeric rearrangement.

It should be noted that solid state intramolecular electron transfer in transition metal complexes does not require significant change of the geometry of coordination polyhedron.[3] In contrast to mentioned above, predicted VT in compound **1** is accompanied by the significant change of coordination geometry (tetragonal pyramidal *vs* tetrahedral). Such structural reconstructions in bis-chelate tin complex **1** can be realized in solution only. Similar considerable transformations of geometry of VT complexes in solutions are known for copper (square planar *vs* tetrahedral)[10a-c] and rhodium (tetragonal pyramidal *vs* trigonal bipyramidal)[10d] *o*-semiquinonates.

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Supporting information, including spectral data, magnetic susceptibility measurements and computational details is given via a link at the end of the document.

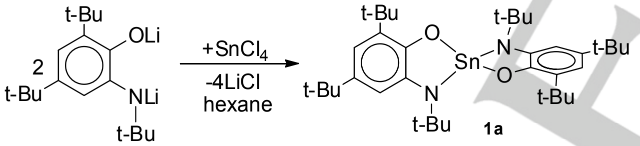
Herein we report the synthesis, characterization and investigation of redox-isomeric properties of bis-chelate tin complex **1** bearing redox-active 4,6-di-*tert*-butyl-*N*-(*tert*-butyl)-*o*-aminophenol ligand.

Results and Discussion

The *tert*-butyl substituted aminophenol APH_2[11] was prepared as white air-stable solid in high 94% overall yield through the modified one-step solvent-free procedure from 3,5-di-*tert*-butylcatechol and *tert*-butyl amine in presence of catalytic amount of iodine.

The bis-chelate complex **1** was prepared by the addition of $SnCl_4$ to a cold hexane solution of $(AP)Li_2$. The latter was prepared from APH_2 and 2 eq. of *n*-BuLi and used *in situ*. The tin ion readily bind 2 eq. of the chelating dianionic ligand $(AP)^{2-}$ giving four-coordinated complex (Scheme 2). The colour of reaction mixture became yellow-green immediately. Compound **1** was isolated in diamagnetic form **1a** as a yellow-orange crystalline solid in 70% yield from the concentrated hexane solution.

According to the single crystal X-ray diffraction analysis, the geometry of coordination polyhedron in **1a** is best described as feebly distorted tetrahedron (Figure 1). The O and N atoms of both AP ligands occupy the tetrahedron vertices. Chelating *o*-amidophenolate ligands have nearly planar geometry. The dihedral angle between two planes of redox-active ligands amounts to 89.94°.



Scheme 2. Synthesis of complex **1**.

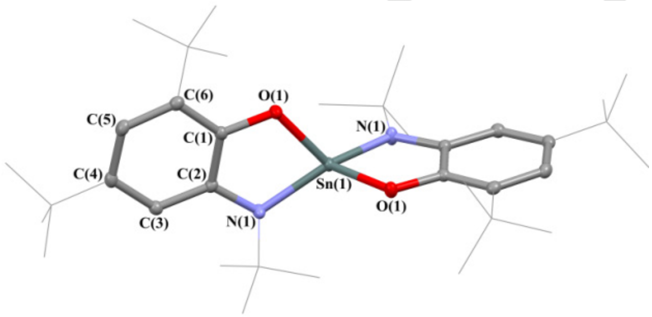


Figure 1. Solid-state structure of the isomer **1a** with 50% thermal probability ellipsoids. The H atoms are omitted for clarity.

The values of Sn(1)–O(1) 1.9697(8) Å and Sn(1)–N(1) 1.9938(9) Å bond lengths are less than the sum of the covalent radii of the corresponding elements (2.09 Å for Sn–O[12], 2.1 Å for Sn–N[12]) and are comparable with those in known *o*-amidophenolate tin compounds.[13] The C(1)–O(1) 1.3670(15) Å, C(2)–N(1) 1.4111(16) Å and C–C distances in the six-membered carbon ring (1.3901(17)–1.4149(17) Å) lie in the range typical for the dianion form of the *o*-iminobenzoquinone ligand. We have performed the analysis of bond lengths for redox-active ligands in **1a** using utility of "metric oxidation state" (MOS) values for assessing bonding in catecholate and amidophenolate ligands.[14] The MOS value obtained for complex **1a** is consistent with the dianion nature of the ligands and amounts to -1.98(6).

Measurements of magnetic susceptibility of crystals of **1a** show no paramagnetism in the range from 300K to 2K that confirms its diamagnetic nature. However, it was found that dissolution of diamagnetic orange crystals of **1a** in non-polar solvents such as toluene (or hexane) leads to intense yellow-green colouring immediately. UV-Vis spectrum of the solution of **1** in toluene displays the intense band at 415 nm and broadened signal in the region of 600-900 nm at room temperature (Figure 2). The presence of wide band at 600-900 nm is characteristic for the metal complexes containing radical-anion *o*-iminosemiquinonato (imSQ) ligands[15,16] and specifies the formation of diradical isomer **1b** (Scheme 1). The results of time-dependent density functional theory (TD-DFT B3LYP/6-311++G(d,p)/SDD) calculations of electron transitions performed by using the Gaussian 09 program package[17] are in accordance with experimental data. The molecular orbital (MO) shapes in **1b** indicate that the long wavelength transitions correspond to intraligand charge transfer (ILCT) combined with a significant metal to ligand charge transfer (MLCT) character, in which the SOMOs and LUMO β-MOs are involved (Figures S1-S2 in Supporting information).

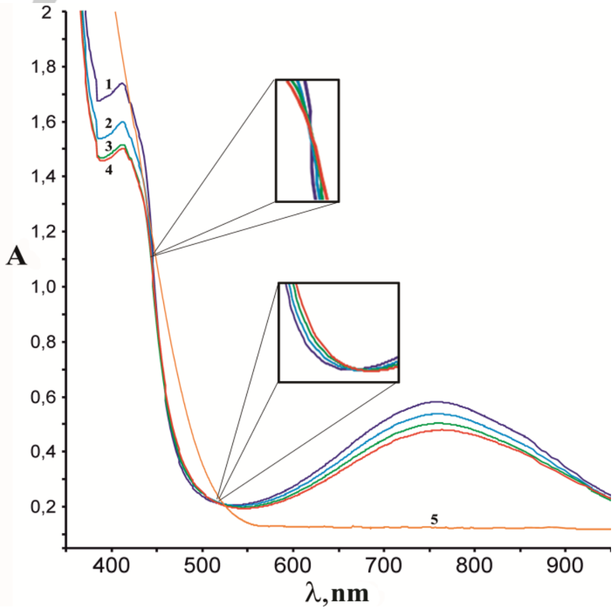


Figure 2. Temperature dependence of the absorption spectrum of **1** in toluene (1 – 293 K, 2 – 323 K, 3 – 343 K, 4 – 363 K). Line 5 is absorption spectrum of compound **2** in pyridine at 293 K (C = $2.0x10^{-3}$ M, L = 1 cm). Insets: isosbestic points at 430 and 520 nm.

The elevation of temperature from 293 K to 363 K is accompanied by decreasing the intensity of these bands and is caused, apparently, by lowering the equilibrium concentration of diradical isomer **1b** in mixture.

The determination of the magnetic susceptibility of **1** in toluene solution using Evans method revealed a value of effective magnetic moment (μ_{eff}) 0.25 μ_B at 313 K. Decreasing the temperature to 223K leads to rising magnetic moment up to 0.87 μB. Observed process is completely reversible (Figure S4 in Supporting information).

The X-band EPR spectrum of the solution of complex **1** in toluene demonstrates the presence of broadened signal at room temperature. In glassy toluene matrix at 150 K EPR spectrum shows features indicative of triplet diradical species (g_{av} = 2.0026) with characteristic half-field (Δm_s = 2) signal (Figure 3). The zero-field splitting parameters are following: D = 22.7x10^{-3} cm^{-1} and E = 4.7x10^{-3} cm^{-1}. These values obtained are comparable with D and E found for tin diradical derivatives.[15] The sharp signal (marked by asterisk), which corresponds to doublet particles, can be explained by association of diradicals **1b** in solution giving rise S = 1/2 species. Such clusterization behavior is well known for such type diradical metal bis-*o*-semiquinolates in non-polar solvents.[18]

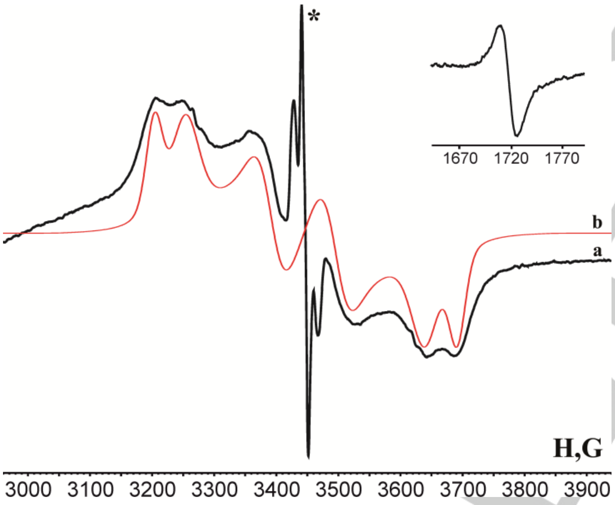


Figure 3. EPR spectra of compound **1** in glassy toluene matrix at 150K (a - experimental, b – simulation; asterisk denotes a doublet species). Inset: half-field region.

The presence of tin ions in different oxidation states (+2 and +4) in toluene solution of compound **1** was unequivocally proved by ^{119}Sn Mössbauer spectroscopy. For the comparison, investigations were carried out both for the crystals of **1a** and for frozen toluene solution of **1**. The Mössbauer spectra at different temperatures are presented in Figure 4 and Figure 5 together with transmission integral fits. The corresponding fitting parameters are listed in Table 1. At 300 K the spectrum of crystals **1a** (Figure 4) could be well reproduced with a single signal at an isomer shift of δ = 0.79(2) mm·s^{-1}, subjected to quadrupole splitting of ΔE_Q = 1.83(2) mm·s^{-1}. The isomer shift lies in the typical range for tetravalent tin.[19]

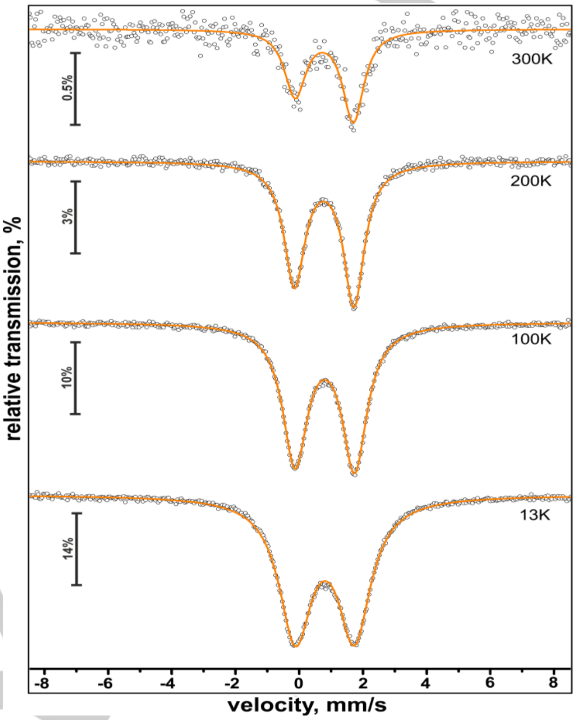


Figure 4. Experimental and simulated ^{119}Sn Mössbauer spectra of the isomer **1a** at various temperatures.

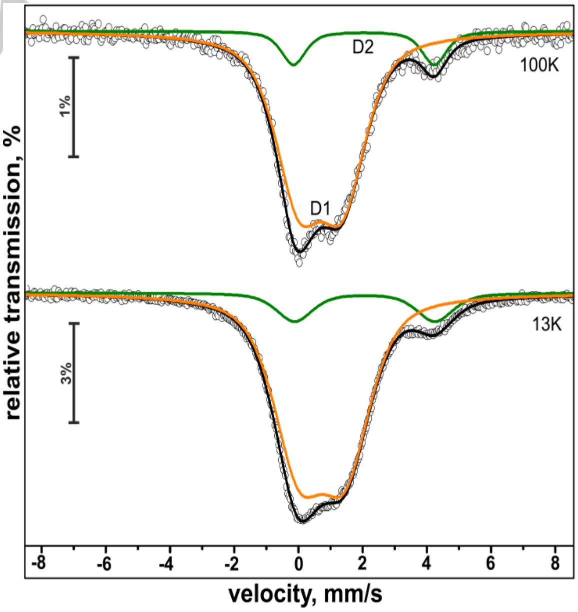


Figure 5. Experimental and simulated ^{119}Sn Mössbauer spectra of frozen toluene solution of **1** at various temperatures.

Observed asymmetry of the corresponding spectrum disappears with decreasing the temperature that is caused by Goldanskii-Karyagin effect.[20] It should be noted, that we did not observe any new signals belonging to tin ions. On the other hand, the spectra of frozen solution of **1** at 13K and 100K (Figure 5) were best reproduced by a superposition of two signals (**D1** and **D2**) with different isomer shifts and quadrupole splitting parameters (Table 1). The **D1** (δ_1 = 0.74(2) mm·s^{-1}) is quite close to signal obtained for crystalline **1a** and is characteristic for Sn^{+4}, while **D2** (δ_2 = 2.07(2) mm·s^{-1}) corresponds to divalent tin derivative.[19] The quadrupole splitting in both cases, as expected, arises from the low site symmetry of the tin ions in **1a** and **1b**.

The relative intensities of the various peaks in Mössbauer spectra reflect the relative concentrations of compounds in a sample and can be used for quantitative analysis. In case of spectra of frozen toluene solution of complex **1**, concentration of the divalent species amounts to 11 %. This value is in a good agreement with results of the magnetic susceptibility measurements using Evans method. The experimental moment can be compared with the spin-only value of 2.45 μB for two uncoupled spins. The share N of available diradicals can be tentatively estimated from equation: $0.87 = 2.45\bullet(N)^{1/2}$, which yields 13% of paramagnetic molecules (at 223K).

Table 1. Fitting parameters of ^{119}Sn Mössbauer spectroscopic measurements of **1** at different temperatures (δ – isomer shift, ΔE_Q – electric quadrupole splitting, G – line weight).

Phase	T, K	component	δ±0.02, mm/s	ΔE_Q ±0.02, mm/s	G±0.02, mm/s
Crystals of **1a**	300	D1	0.79	1.83	0.81
	200	D1	0.79	1.87	0.80
	100	D1	0.80	1.87	0.94
	13	D1	0.81	1.85	1.25
Frozen solution of **1**	100	D1	0.69	1.39	1.83
		D2	2.04	4.38	0.92
	13	D1	0.74	1.47	1.88
		D2	2.07	4.37	1.36

Data obtained indicate that dissolution of diamagnetic compound **1a** in toluene is accompanied by occurrence of redox-isomeric rearrangement with the formation of **1b** comprising tin ion in oxidation state +2 and ligands in *o*-iminosemiquinonate form (Scheme 1). Noteworthy that previous quantum-chemical calculations[8] suggested that the diradical **1b** should be more preferable than the pseudotetrahedral diamagnetic **1a**. However, as we can see, in a frozen matrix the distribution of the diradical structure amounts to only 11%. We suppose that the formation of diradicals is not favored entropically due to intermolecular interaction between them which leads to association of diradicals with subsequent lowering of the entropy of the system. It shifts the equilibrium (Scheme 1) to the diamagnetic form **1a**. The fact of association of related diradical metal complexes in non-polar solvents is well known in the literature[18]. Moreover, mentioned above observation of signals from S=1/2 species in EPR spectra can indirectly confirm this hypothesis.

We can assume two possible mechanisms for this interconversion of paramagnetic **1b** into diamagnetic **1a**. The repulsion of two sterically hindered *o*-iminosemiquinonate ligands and a lone pair of tin(II) leads to the distortion of the initial pyramidal geometry to the pseudotetrahedral one (through predicted by calculations[8] MECP geometry). Such rearrangement causes the electron transfer from the divalent metal to radical-anion ligands. The alternative route includes oxidation of the low valent tin center by two iminosemiquinone ligands in **1b** which leads to the formation of tin(IV) compound. The last stabilizes as a tetrahedron. It has to be mentioned that the unequivocal choice of the mechanism of this redox-isomeric interconversion needs the additional investigations.

It was found that dissolution of **1** in pyridine leads to conversion of the solution colour from yellow-green to intense orange and the subsequent full disappearance of any radical signal in EPR spectrum. The UV-Vis spectrum does not demonstrate characteristic broadened signal at 600-900 nm (Line 5 in Figure 2). All these alterations are caused by the formation of new octahedral diamagnetic tin complex **2** (Scheme 3). According to the computational results, absorption in the area of 500 nm corresponds to the band of charge transfer from *o*-amidophenolate ligand to pyridines (LLCT) (Figure S3 in Supporting information).

Single crystals of complex **2** suitable for X-ray diffraction analysis were obtained from saturated pyridine solution. In solid state, compound **2** shows a distorted octahedral coordination geometry composed of the O and N atoms of two AP ligands and N(3) and N(4) atoms of coordinated pyridine molecules (Figure 6). The dihedral angle between two redox-active ligands amounts to 72.14°. The C-O, C-N, Sn-O and Sn-N bond lengths in chelating fragments are comparable with *o*-amidophenolate tin structure **1a** and confirm its dianionic nature.[13] Two pyridine molecules have *cis*-spatial arrangement in the complex **2**. The values of Sn(1)–N(3) 2.3385(11) Å and Sn(1)–N(4) 2.3624(11) Å distances are larger than the sum of the covalent (2.12 Å)[12] but significantly less than the sum of the van-der-Waals (3.8 Å)[12] radii of corresponding elements. It indicates its donor–acceptor bonding character.

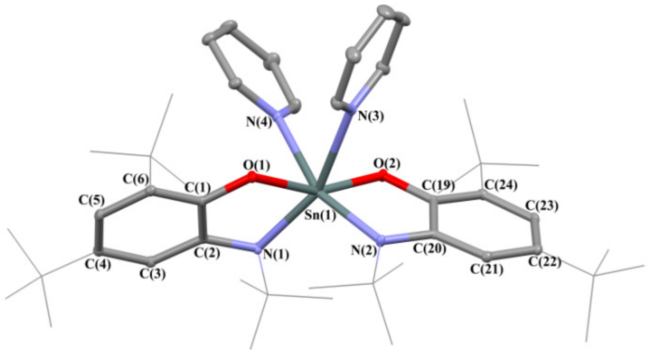


Figure 6. Solid-state structure of complex **2** with 50% thermal probability ellipsoids. The H atoms and lattice solvent molecules are omitted for clarity. Selected bond lengths [Å]: C(1)-O(1) 1.3649(15), C(19)-O(2) 1.3620(15), C(2)-N(1) 1.3991(16), C(20)-N(2) 1.3943(16), Sn(1)-O(1) 2.0182(9), Sn(1)-O(2) 2.0251(9), Sn(1)-N(1) 2.0769(10), Sn(1)-N(2) 2.0790(11).

$$\underset{\mathbf{1b}}{(imSQ)_2Sn^{II}} \xrightleftharpoons{\text{toluene}} \underset{\mathbf{1a}}{(AP)_2Sn^{IV}} \xrightarrow{\text{Py}} \underset{\mathbf{2}}{(AP)_2Sn^{IV}(Py)_2}$$

Scheme 3. Transformations of complex **1** in different solvents.

Complex **2**, which does not undergo redox-isomeric transformations, is the only product of the interaction of electromers **1a** and **1b** with pyridine (Scheme 3). It should be noted that the formation of compound **2** is irreversible: a heating of the solution up to 353 K does not result in dissociation of this complex into initial components. It is confirmed by the results of calculations (DFT B3LYP/6-311++G(d,p)/SDD)) pointing to the energy preference of **2** by 17 kcal·mol^{-1} as compared to the sum of energies of isolated tetrahedral isomer **1a** and two pyridine molecules (Table S1 in Supporting information). Compound **2** can be recrystallized from toluene without losing solvated pyridine molecules. It should be noted that the effect of added donor ligands on the distribution of redox states between ligand and metal center is known in the literature.[21]

Conclusions

In summary, bis-chelate tin complex **1** bearing 4,6-di-*tert*-butyl-*N*-(*tert*-butyl)-*o*-aminophenol ligands is the first non-transition metal compound, which demonstrates the redox-isomerism phenomenon. This compound exists in non-polar solvents as an equilibrium mixture of two different isomers – diamagnetic pseudotetrahedral $(AP)_2Sn^{IV}$ and paramagnetic tetragonal-pyramidal structure of low-valence tin $(imSQ)_2Sn^{II}$. This process can be quenched by an addition of strong donor ligand resulting in an octahedral complex **2** which does not undergo reversible intramolecular electron transfer. This work can be regarded as a starting point in investigations of unexplored field of redox-isomerism in main group chemistry.

Experimental Section

General considerations: All reactants were purchased from Aldrich. Solvents were purified by standard methods.[22] All manipulations on complexes were performed under vacuum conditions, in which oxygen and moisture were excluded. EPR spectra were recorded by using a Bruker EMX spectrometer (working frequency ≈ 9.75 GHz). The g_i values were determined using 2,2-diphenyl-1-picrylhydrazyl (DPPH) as the reference (g_i = 2.0037). EPR spectra were simulated using Easyspin toolbox for Matlab.[23] NMR spectra were recorded by using a Bruker Avance III 400 MHz instrument with TMS as an internal standard. The signals in the NMR spectra were assigned using 2D ge-COSY and ge-HSQC procedures. Solution magnetic susceptibility for complex **1** was determined by Evans method[24] using Bruker Avance III 400 NMR spectrometer. UV-VIS spectra were obtained on a Perkin Elmer λ 25 spectrometer. ^{119}Sn Mössbauer spectra were recorded at MS1104Em spectrometer by using $Ca^{119m}SnO_3$ as a source. The measurements were conducted in the usual transmission geometry in the temperature range from 13 to 300 K with a total counting time of up to 1 day per spectrum. The magnetic susceptibility of the polycrystalline complex **1a** was measured with a Quantum Design MPMS*XL* SQUID magnetometer in the temperature range 2-300 K with magnetic field of up to 5 kOe.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1472088 and 1472089 for compounds **1a and 2•2Py** respectively.

Synthesis of 4,6-di-*tert*-butyl-N-(*tert*-butyl)-*o*-aminophenol (APH_2): Ampoule was charged with 3,5-di-*tert*-butylcatechol (5 g, 22.5 mmol) and 2,5 ml of tert-butyl amine was added. 0.28 g (5% mol) of I_2 was entered into the reaction. Reaction mixture was kept for a 4 hours at 120°C (melting point of 3,5-di-*tert*-butylcatechol). The colour of reaction mixture became brown. The residue was twice recrystallized from hot acetonitrile. APH_2 was obtained as a white crystalline product. Yield: 5.9 g (94%).

Synthesis of bis-(4,6-di-*tert*-butyl-N-(*tert*-butyl)-*o*-amido-phenolato)tin(IV) (1a): A frozen hexane solution (20 ml) of $APLi_2$, generated from 0.34 g of APH_2 (1.2 mmol) and 2 equiv of *n*-BuLi in hexanes, was thawed and $SnCl_4$ (0.156 g, 0.6 mmol) was added. The reaction mixture was allowed to warm to room temperature and then was kept for 1 h. Reaction mixture became intense yellow-green. A white precipitate of LiCl byproduct was removed by filtration. Solution was concentrated twice (10 ml). Complex **1** was isolated in diamagnetic **1a** form as a yellow-orange crystalline solid in 70% yield from hexane solution. Yield: 0.28 g (70%). $C_{36}H_{58}N_2O_2Sn$. Calculated C 64.58, H 8.73, N 4.18, Sn 17.73; found C 64.54, H 8.78, N 4.23, Sn 17.78. ^{1}H NMR (toluene-d_8, J/Hz, 20°C): δ = 7.14 (d, 2H, $J_{H,H}$ = 2.1, H_{AP}); 7.06 (d, 2H, $J_{H,H}$ = 2.1, H_{AP}); 1.67 (s, 18H, *t*-Bu); 1.42 (s, 18H, *t*-Bu); 1.37 (s, 18H, N-(*t*-Bu)) ppm. ^{13}C NMR (toluene-d_8, 20°C): δ = 144.7, 140.2 (C-(*t*-Bu)); 135.9 (C-O); 135.6 (C-N); 112.2, 109.5 (C_{aryl}); 54.1 (N-C_{quat}); 35.2, 34.4 (C_{quat}); 31.7, 31.4, 29.7 (CH_3(*t*-Bu)) ppm.

Synthesis of bis-(4,6-di-*tert*-butyl-N-(*tert*-butyl)-*o*-amidophenolato)tin(IV) bis-pyridinate (2): Complex **1a** (0.28g 0.42 mmol) was dissolved in an excess of pyridine (20 ml). The reaction mixture became intense orange. Solution was concentrated twice (10 ml). Complex **2** was isolated as orange crystals in 85% yield. Yield: 0.29 g (85%). $C_{46}H_{68}N_4O_2Sn$. Calculated C 66.74, H 8.28, N 6.77, Sn 14.34; found C 66.71, H 8.25, N 6.81, Sn 14.38. ^1H NMR (C_6D_6, J/Hz, 20 °C): δ = 8.69 (dd, 4H, $J_{H,H}$ = 1.5, $J_{H,H}$ = 4.6, H_{py}); 7.22 (d, 2H, $J_{H,H}$ = 2.1, H_{AP}); 6.96 (d, 2H, $J_{H,H}$ = 2.1, H_{AP}); 6.65 (tt, 2H, $J_{H,H}$ = 1.5, $J_{H,H}$ = 7.7, H_{py}); 6.35 (m, 4H, H_{py}); 1.77 (s, 18H, *t*-Bu); 1.67 (s, 18H, *t*-Bu); 1.44 (s, 18H, N-(*t*-Bu)) ppm. ^{13}C NMR (C_6D_6, 20 °C): δ = 148.5 (C_{Py}); 145.5, 139.7 (C-(*t-Bu*)); 138.0 (C_{Py}); 137.6 (C-O); 132.2 (C_{Py}); 123.5 (C-N); 110.6, 108.4 (C_{aryl}); 53.9 (N-C_{quat}); 34.9, 34.4 (C_{quat}); 32.0 (CH_3(t-Bu)); 31.0, 30.5 (CH_3(t-Bu)) ppm. ^{119}Sn NMR (C_6D_6, 20 °C): δ = -451.4 ppm.

Acknowledgements

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Keywords: redox-isomerism • redox-active ligand • iminoquinone • tin complex• Mössbauer spectroscopy

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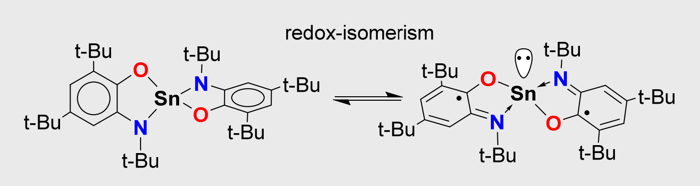

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Redox-isomerism in main group chemistry: tin complex with o-iminoquinone ligands

Bis-chelate tin complex bearing redox-active *o*-aminophenol ligand representing the first example of redox-isomeric compound in main group chemistry was synthesized and investigated. This complex exists in non-polar solvents as an equilibrium mixture of two different isomers – diamagnetic pseudotetrahedral tin(IV) compound and paramagnetic tetragonal-pyramidal structure of tin(II).